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Gas Chromatographic Determination of Aviation Gasoline and JP-4 Jet Fuel in Subsurface Core Samples (Journal Version)

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Gas Chromatographic Determination of Aviation Gasoline and JP-4 Jet Fuel in Subsurface Core Samples

Steve A. Vandegrift
Northrop Services, Inc., Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, Oklahoma 74820

Don H. Kampbell
U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, Oklahoma 74820

Abstract

A new gas chromatographic procedure for quantifying levels of aviation gasoline (avgas) and JP-4 jet fuel contamination in soils is described. The fuel is extracted from a small quantity of soil or subsurface material, typically about 6 g, using 3 mL of methylene chloride. The extract is analyzed by wide-bore capillary column gas chromatography with flame ionization detection. Advantages of the method are (1) a short analysis time of 20 minutes, (2) the use of small amounts of solvent, (3) detection limit in the low parts-per-million range, and (4) determination of the type of fuel contamination (i.e., avgas or jet fuel) by the chromatographic pattern or "fingerprint."

Introduction

Serious environmental problems can result from petroleum fuel leaking from underground storage tanks and pipelines. Upon reaching the groundwater, the fuel can spread and migrate downgradient. Sampling within and beyond the plume has to be done to assess the extent of contamination.

Petroleum constituents are held by surface tension as globules within the open capillaries in the unsaturated zone of the solid subsurface material. Water samples from the plume primarily indicate the presence of BTXs (benzenes, toluenes, xylenes), which basically have a higher water solubility than the other components in jet fuel or aviation gasoline. The total amount of BTXs and other organics in the subsurface needs to be known to implement in situ biorestoration methodology. To accomplish this, aseptic core samples were collected at various depths by special drilling tools.

U.S. Environmental Protection Agency Methods 602 (1), 5030, and 8020 (2) are available to determine purgeable aromatics in water and solid wastes. Method 3820 (2) uses a hexadecane extraction, where the soil or sediment is first extracted with water, then the water is extracted with hexadecane. Therefore, only water soluble components would be analyzed. Qualitative and quantitative analysis of hydrocarbon-fuel-contaminated groundwater has been described (3–5), with some procedures using solvent extraction (6–8).

Our need was for an analytical method to determine both volatile and semivolatile aviation gasoline and JP-4 jet fuel hydrocarbons in core samples. It was determined that a solvent extraction of the core material gave the results needed.

Experimental

Sample preparation

Subsurface samples were cored with a specially designed drillpipe. The core material, a uniform fine-to-medium grain sand, was extruded from the pipe into quart glass jars inside a nitrogen atmosphere glovebox. The jars were capped with air-tight lids before removal from the glovebox (9).

In the laboratory, core subsamples for analysis were quickly taken from the sample jar with an 8-mm i.d. paste sampler (American Scientific Products) modified with a Teflon gasket to prevent sample loss. The subsample was extruded into a tared 22-mL headspace vial that contained 5 mL of organic-free water. The water provided good solvent wetting of the core material. The vial was sealed with a Teflon-lined septum cap. Three milliliters of pesticide-residue grade methylene chloride (Burdick & Jackson) was injected through the septum. The vial was rotary shaken (Tekmar VXR Vibrax, Thomas Scientific) for 15 min, then sonicated in an ultrasonic bath (Varian-Aerograph) for several minutes to break up any emulsion. At least 1 mL of the solvent phase was passed through a microcolumn of anhydrous sodium sulfate. The eluate was collected in a 2-mL vial, capped, and stored at 4°C for subsequent analysis.

Gas chromatography

One microliter of the dried extract was injected into a Hewlett-Packard 5880 GC. The injection was done in a splitless mode with a solvent purge at 0.7 min. Both the injector and the flame ionization detector (FID) were at 300°C. A wide-bore capillary column was used: J&W Scientific (DB-5) cross-linked 5% phenyl methyl silicone 15 m × 0.53 mm i.d., 1.5-μm film thickness. High-purity helium was used as a carrier at 9 mL/min, 45°C. High-purity nitrogen was used as the FID makeup gas at 21 mL/min. The GC oven was cooled cryogenically by liquid nitrogen. The oven was temperature programmed: 10°C, 3-min hold, 10°C/min to 225°C, 2-min hold.

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Quantitation

JP-4 jet fuel and avgas were obtained from a local refinery. Standards were prepared by adding measured aliquots of JP-4 jet fuel or aviation gasoline to methylene chloride. A calibration curve was prepared by analyzing known amounts and summing the areas of the major peaks for each standard concentration. The curves are shown in Figures 1 and 2.

Some variability can exist with refineries and feedstock. It is best to obtain the fuel from the refinery from which the contaminating fuel originated. Better yet, if possible obtain the fuel from the actual source, for example, storage tank or pipeline. It is important that the type of fuel involved is known before attempting to quantify with this method. Otherwise, results may be misleading.

Retention times of the major peaks used for each calibration standard or sample analyzed are listed in Tables I and II. Also listed in Tables I and II are the names of the compounds identified by gas chromatography/mass spectrometry (GC/MS). Analysis was performed on a Finnigan 4500 GC/MS, Incos 2000 data system, splitless injection using a 28-m × 0.32-mm i.d. DB-5 column (J&W Scientific).

Results were reported in units of micrograms of aviation gasoline or JP-4 jet fuel per gram of wet core material. A nominal value of 85% (w/w) carbon (as determined by a C-H-N analysis of the fuels) was used to convert fuel quantity to micrograms of fuel carbon per gram of core material. One sample in every 10 was spiked and one in every 10 was analyzed in triplicate.

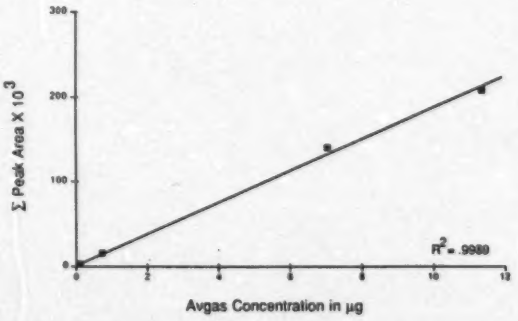

Figure 1. Standard calibration curve for aviation gasoline.

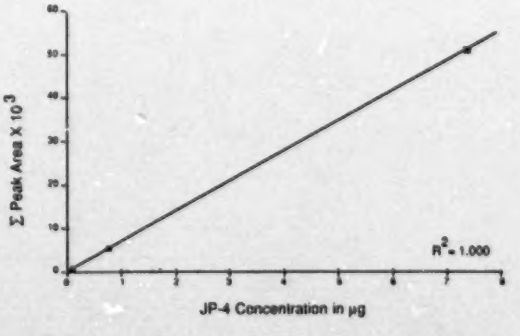

Figure 2. Standard calibration curve for JP-4 jet fuel.

Results and Discussion

Uncontaminated or "blank" core material and core samples were spiked with known amounts of JP-4 jet fuel and aviation gasoline. The blank core material was from the same aquifer, but outside the area contaminated by the avgas plume. Recovery data obtained is listed in Table III. Precision data of the spikes is also provided as coefficient of variation (CV).

The blank core material gave consistently better recovery efficiencies and precision values. This was attributed to the heterogeneity of the contaminated samples. The recovery efficiency was determined by comparing the concentration of an unspiked sample with a spiked sample. If the background level

Table I. Aviation Gasoline Chromatogram Peaks Selected for Calibration

Peak number	Retention time (min)	Compound
1	2.47	2,4-Dimethylpentane
2	3.48	2,3-Dimethylpentane
3	3.98	2,2,4-Trimethylpentane
4	5.19	2,4-Dimethylhexane
5	5.64	2,3,4- and 2,3,3-Trimethylpentane
6	5.94	Toluene and 2,3-dimethylhexane
7	6.41	2,2,4- and 2,2,5-Trimethylhexane

Table II. JP-4 Jet Fuel Chromatogram Peaks Selected for Calibration

Peak number	Retention time (min)	Compound
1	3.46	2-Methylhexane
2	4.37	Heptane
3	5.94	Toluene
4	6.04	3-Methylheptane
5	6.21	1,3-Dimethylcyclohexane or 1,4-dimethylcyclohexane
6	6.84	Octane
7	7.47	Tetramethylcyclopentane or trimethylcyclohexane
8	8.25	*m*-Xylene and *p*-xylene
9	8.97	Nonane
10	10.13	Trimethyloctane
11	10.86	Decane
12	12.58	Undecane
13	14.18	Dodecane
14	15.68	Tridecane
15	17.07	Tetradecane

Table III. Accuracy and Precision of Spiked Samples as Percent Recovery and Coefficient of Variation

Aviation gasoline		JP-4 jet fuel	
Blank core material % recovery	Core samples % recovery	Blank core material % recovery	Core samples % recovery
89.8	69.4	100	89.9
89.4	101	93.1	95.6
90.0	—	101	73.5
93.8	—	95.9	76.6
$\bar{x}$ 90.8	85.2	97.5	83.9
CV 2.26	26.2	3.76	12.6

in the spiked sample varied significantly from the unspiked sample, the percent recovery would vary accordingly.

Chromatographic separation of the fuel components is shown in Figures 3 through 6. The similarities between the standard and sample chromatograms are apparent. The solvent peak of methylene chloride eluted between 1 and 2 min during the 20-min run.

Linear regression values (R^2) shown in Figures 1 and 2 indicate a very good linear fit of peak area summation to fuel concentration. The range of standard concentrations used encompassed the sample concentrations. Limit of detection for a 5-g sample was near 20 μg carbon per gram core material for a 1-μL extract injection. Detection limits varied depending on weight of sample extracted.

Conclusion

The GC method provided a rapid, accurate, and precise quantitative analysis of subsurface core materials for aviation gasoline and JP-4 jet fuel. The method, referred to as FC/GC (fuel carbon by gas chromatography), will be used at our facility to analyze fuel contamination subsurface soil samples.

Disclaimer

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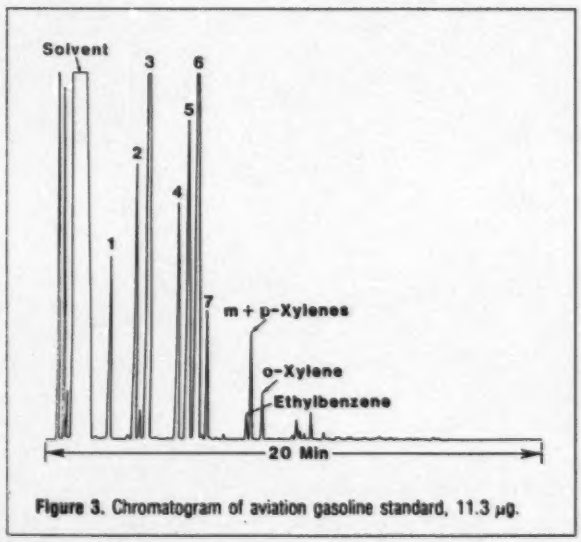

Figure 3. Chromatogram of aviation gasoline standard, 11.3 μg.

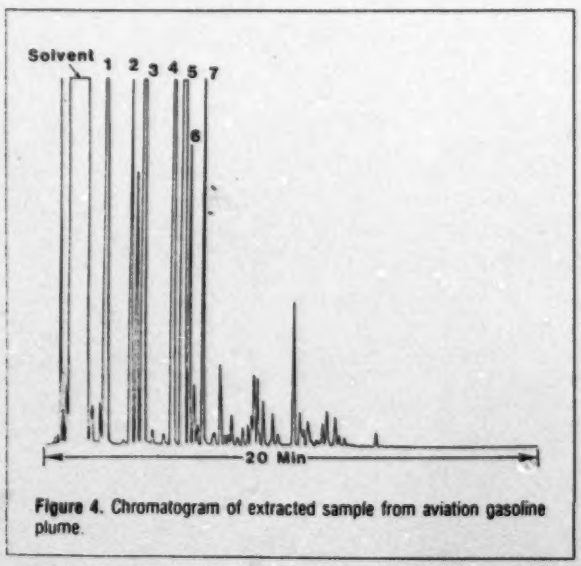

Figure 4. Chromatogram of extracted sample from aviation gasoline plume.

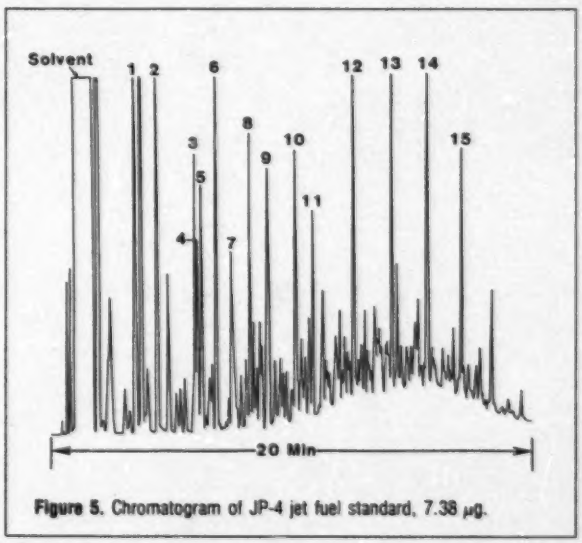

Figure 5. Chromatogram of JP-4 jet fuel standard, 7.38 μg.

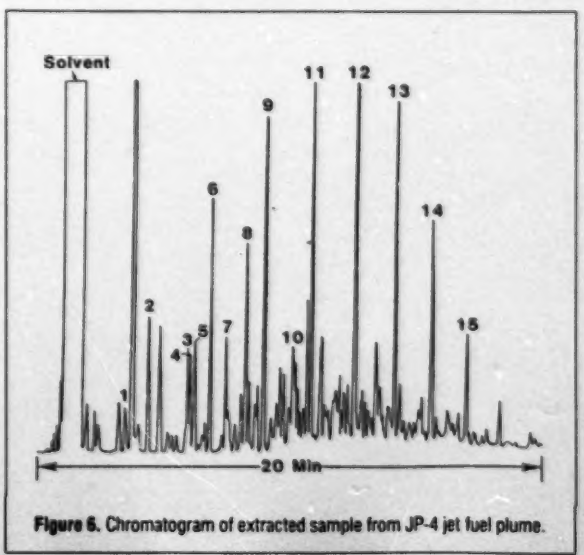

Figure 6. Chromatogram of extracted sample from JP-4 jet fuel plume.

of the figures. The authors are also very grateful for the GC/MS analysis provided by Garmon Smith.

References

1. *Fed. Regist.* **49(209)**: 40–48 (Oct. 26, 1984).
2. *Test Methods for Evaluating Solid Waste.* U.S.E.P.A., SW-846, Sept. 1986.
3. K. Petrovic and D. Vitorovic. Recognition and qualitative characterization of commercial petroleum fuels and synthetic fuels by a gas chromatographic fingerprinting technique. *J. Chromatogr.* **119**: 413–22 (1976).
4. C. Bruell and G. Hoag. Capillary and packed-column gas chromatography of gasoline hydrocarbons and EDB. In the proceedings of the NWWA Conference, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration, 1984.
5. G. Hoag, C. Bruell, and M. Marley. *A Study of the Mechanisms Controlling Gasoline Hydrocarbon Partitioning and Transport in Groundwater Systems.* Institute of Water Resources, University of Connecticut, 1984.
6. A. Roberts and T. Thomas. Characterization and evaluation of JP-4, Jet A and mixtures of these fuels in environmental samples. *Environ. Toxicol. Chem.* **5**: 3–11 (1986).
7. R. Senn and M. Johnson. Interpretation of gas chromatography data as a tool in subsurface hydrocarbon investigations. In the proceedings of the NWWA Conference, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Restoration, 1985.
8. R. Cooper, L. Hunter, P. Ulrichs, and R. Okazaki. *Environmental Quality Research—Fate of Toxic Jet Fuel Components in Aquatic Systems.* University of California, 1981.
9. L. Leach, F. Beck, J. Wilson, and D. Kampbell. *Aseptic Subsurface Sampling Techniques for Hollow-Stem Auger Drilling,* in preparation.

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